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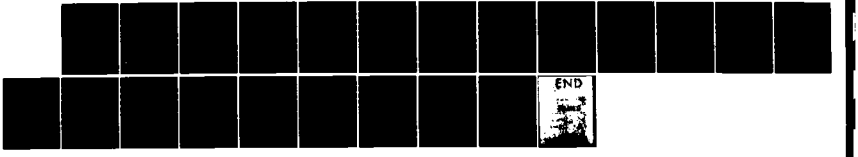

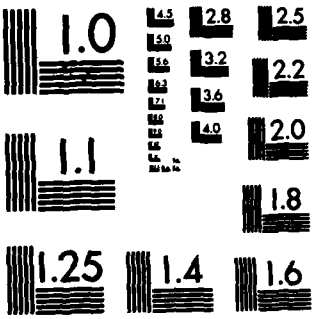

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COMBUSTION CHEMISTRY OF VIBRATIONALLY EXCITED OXYGEN

FINAL REPORT

Richard B. Miles
Jack Gelfand
Herschel Rabitz

July 1984

U. S. Army Research Office
Contract DAAG29-82-K-0046

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We are investigating the use of stimulated resonance Raman pumping to prepare oxygen in selected vibrational states of the ground electronic manifold. This necessitates the development of a laser source capable of producing radiation in the region of the Schumann-Runge transition of O_2 near 200 nm. We have generated this radiation utilizing a quadrupled YAG laser shifted in a high pressure H_2 Raman cell. This laser output was made tunable by employing an intracavity etalon in the YAG laser oscillator. Utilizing this source we have produced photoacoustic spectra in the Schumann-Runge band and have observed

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resonance fluorescence to excited vibrational states of the electronic ground state. We are currently undertaking a series of spectral measurements to determine the relative strengths of predissociation, fluorescence and resonant Raman as a function of the wavelength of the exciting laser.

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1. INTRODUCTION

We have explored the use of stimulated resonance Raman (SRR) pumping to prepare oxygen in selected vibrational states of the ground electronic manifold. The purpose of this experiment is to produce highly vibrationally excited oxygen in order to investigate its reaction chemistry with selected hydrocarbons. The stimulated resonance Raman pumping technique has been proposed by DePristo, Rabitz, and Miles [1] as an effective method for selectively populating the higher vibrational states of molecules. Highly vibrationally excited molecules have been produced by direct overtone pumping of vibration-rotation transitions. However, due to the fact that oxygen is a homonuclear molecule direct absorption cannot be used to vibrationally excite it. Stimulated Raman scattering may be used to populate the first vibrationally excited state as has been done by Frey, Lukasik and Ducuing [2]. Due to selection rules, higher lying vibrationally excited states may not be prepared with the stimulated Raman technique. It is well known that the Raman selection rules break down when the incident photon lies near an allowed electronic transition. The Raman selection rules are replaced by the Franck-Condon overlap factors which typically couple a wide range of vibrational transitions [3]. In addition, the Raman cross sections increase due to strong resonance enhancement. SRR pumping, therefore, may be used to selectively excite a wide range of vibrational states.

During the two year period of this contract, we concentrated on developing the appropriate ultraviolet wavelength sources needed in the SRR pumping scheme, and in doing some initial experiments to elucidate the problems we would encounter. This necessitated the use of a hydrogen Raman shifter with a quadrupled Nd:YAG laser. With this system we were successful in generating

a number of wavelengths in the Schumann-Runge transition region. We also set up a photoacoustic detection cell and tested it for detecting absorption of VUV radiation by oxygen. We found that because the Schumann-Runge transition is predissociated an interfering signal was created by the production of ozone following the dissociation of oxygen into oxygen atoms. This made it difficult to detect whether the stimulated resonance Raman process was taking place using the photoacoustic technique. As an alternative, we are presently investigating the resonance overtone Raman scattering by standard Raman methods in order to learn more about the wavelength dependence of resonance enhancement.

2. EXPERIMENTAL APPROACH

The most important experimental consideration is finding an appropriate electronic state to use in the stimulated resonance Raman pumping process that is accessible with a practical laser system. In oxygen, the longest wavelength allowed electronic transition is in the 200 nm region. This is known as the Schumann-Runge band and is a transition from the ground electronic state to the $^3\Sigma_u$ state. In the pumping scheme that we are investigating we attempt to use one laser pulse whose wavelength is tuned near a transition in the Schumann-Runge band and another which stimulates a Raman transition to a upper vibrational state of the ground electronic state. This scheme is diagrammed in Figure 1. In room temperature oxygen practically all of the molecules occupy the ground vibrational state, $v'' = 0$. To prepare an excited vibrational state in the ground electronic state, $v'' = n$, we will utilize a vibration-rotation state in the electronically excited $^3\Sigma_u$ state which couples both with $v'' = 0$ and $v'' = n$. Two lasers are used as shown in Figure 1. One takes the molecule from the ground state to a virtual state near a vibronic state of $^3\Sigma_u$, and the second returns it to the desired vibrational state of the ground manifold.

We have investigated a number of overlaps between readily available laser sources and appropriate transitions in the Schumann-Runge bands. These are summarized in Table 1. The most convenient overlap shown in this table is with the output of an ArF excimer laser for transitions from the ground $v'' = 0$ state to the $v' = 4$ vibronic state in the $^3\Sigma_u$ manifold. It would be possible utilizing various types of doubled dye laser configurations to access a number of highly vibrationally excited states in the ground electronic state of oxygen using an ArF laser as the up-pumping source. However, for reasons

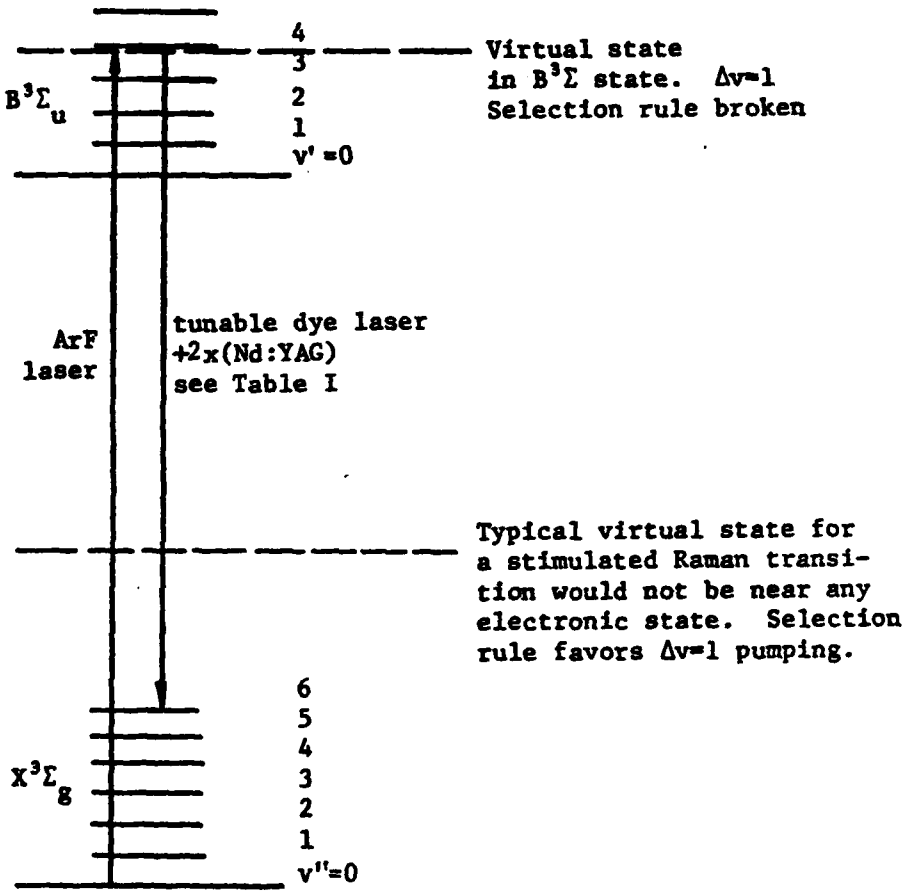


Figure 1 Proposed pumping scheme for excitation of high lying vibrational states of the electronic ground state of O_2.

which will be outlined later, these transitions were found to be inappropriate because of the predissociation of this electronic state which dissociates the oxygen into oxygen atoms and has been found to be a maximum for the $v' = 4$ state accessed by the ArF laser. A further investigation of the transitions in the Table 1 indicates that the most appropriate transition which is easily accessed with readily available laser sources is the transition to the $v' = 1$ vibronic state in the Schumann-Runge band. This state can accessed by a laser source generated from three hydrogen Raman shifts of the output of a quadrupled Nd:YAG laser. This transition is to a state that has much less predissociation than the state accessed by the ArF excimer laser. Another transition which would be favorable is that which could be accessed with a quadrupled YAG laser, five times Raman shifted in HD. However, we were not successful in generating significant power at this wavelength.

The experimental setup which was used in this investigation is shown in Figure 2. 700 mJ of 1.06 micron radiation is generated by the Molectron YAG laser oscillator-amplifier. The most important aspect of this setup is the inclusion of an intracavity etalon to obtain up to 3 cm^{-1} tunability over the gain curve of the Nd:YAG oscillator. The output of the amplifier is doubled and then doubled again to provide twelve wavenumbers of tunable radiation at 266 nm. This output is then passed into a high pressure H_2 Raman shifter. From this Raman shifter we obtain a number of anti-Stokes output lines and one can note from Table 1 that one of these output lines is coincident with the R(1) and R(3) transisions in the 1-0 band of the Schumann-Runge transition. A portion of the photoacoustic spectrum that can be obtained when tuning the YAG laser in this region is shown later in this report.

The tunable output of the laser system in the 200 nm region was used for two experiments. The output was directed to a photoacoustic cell whose

Table I. Table of the wavenumbers of Raman shifted Nd:YAG laser lines and the ArF laser line and possible O_2 Schumann-Runge vibronic transitions.

Gas	Shift	Wavenumber (vac)	$^{16}O_2$ Absorption Lines Wavenumbers (vac)
H_2[a]	3 AntiStokes	50045.0 cm^{-1}	1-0 R(5) 50036.2 1-0 P(1) 50042.9 1-0 R(3) 50044.5 1-0 R(1) 50047.3
H_2[a]	4 AntiStokes	54200.2 cm^{-1}	9-0 P(21) 54232.3 9-0 P(21) 54231.5 9-0 R(23) 54219.5 9-0 R(23) 54218.6 9-0 P(23) 54158.9 9-0 P(23) 54157.9
HD[a]	4 AntiStokes	52092.5 cm^{-1}	5-0 R(25) 52143.6 5-0 P(23) 52141.0 5-0 R(27) 52083.0 5-0 P(25) 52068.8
HD[a]	5 AntiStokes	55720.3 cm^{-1}	12-0 P(7) 55727.7 12-0 P(7) 55727.2 13-0 P(19) 55718.4 13-0 P(19) 55717.4 12-0 R(7) 55717.2 12-0 R(9) 55716.2 13-0 P(19) 55715.2 12-0 P(9) 55695.7 12-0 P(9) 55695.1
ArF[b]	193 nm line	51720.0 cm^{-1}	4-0 P(15) 51783.02 4-0 P(17) 51735.19 4-0 P(19) 51681.43 4-0 R(17) 51787.24 4-0 R(19) 51740.35 4-0 R(21) 51687.20

[a] The etalon in the YAG laser used to generate this UV light allows one to tune approximately ±3 cm^{-1} from the center wavenumber shown.

[b] With appropriate injection locking from another laser source one can tune the ArF laser over all the lines shown.

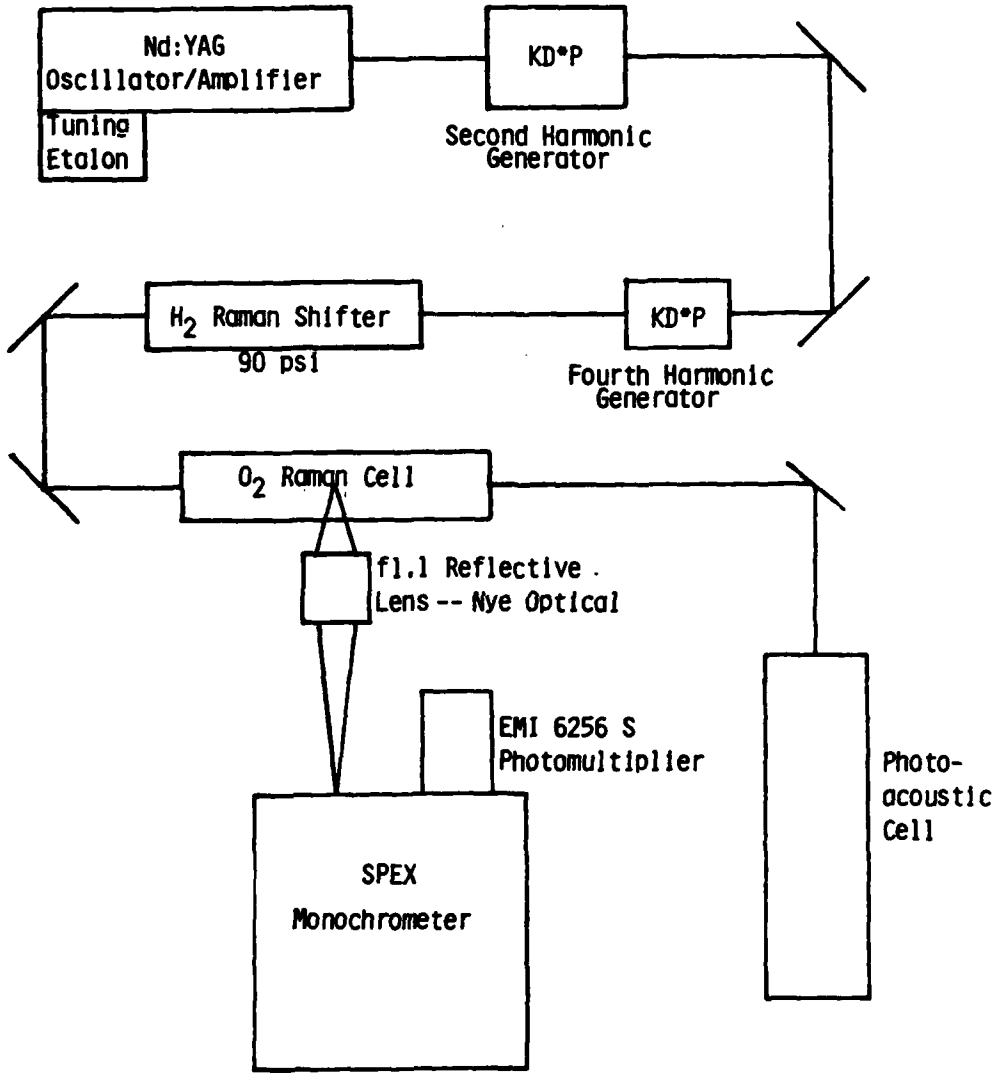


Figure 2. Experimental setup used for generating tunable 200 nm radiation and performing the fluorescence, Raman and photoacoustic measurements described in the text.

construction was discussed in detail by Rohlfing et al. [4]. We utilized this photoacoustic cell to evaluate the wavelength range and tunability of the shifted YAG laser system. The output of the laser system was also directed into a Raman cell in which we have evaluated the fluorescence from oxygen when pumped in the 200 nm range. The photoacoustic cell can be used in conjunction with the Raman cell to determine the wavelength of the exciting radiation. The Raman cell has quartz windows and the light is focused into the cell with a 50 cm focal length lens, providing a beam waist at the center of the cell of approximately 500 μm. The light was collected with a two element all-reflective optical element and directed into a Spex 1.5 meter spectrograph. Because the exciting laser is tuned onto a transition in the Schumann-Runge band this light is probably fluorescence from O_2. These results will be detailed in the next section.

3. EXPERIMENTAL RESULTS

It was our original intention to investigate the feasibility of the stimulated resonance Raman pumping technique by utilizing the photoacoustic detection technique to provide an indication of absorbed power from the two SRR laser sources. It is necessary in this experiment to tune the up-pumping laser to a wavelength near a vibronic transition in the Schumann-Runge bands and then to tune the second down-pumping laser to an appropriate wavelength to initiate a stimulated resonance Raman transition to a vibrationally excited state of the ground electronic state. We first tested the range and tunability of the up-pumping laser utilizing the photoacoustic technique to obtain photoacoustic spectra of a transition in the Schumann-Runge bands. This was the R(3) transition in the 1-0 vibronic band. We directed the 200 nm radiation into the photoacoustic cell and used a boxcar signal averager tuned to the first acoustic resonance of the photoacoustic cell and plotting the magnitude of the photoacoustic signal as a function of the wavelength of the tunable YAG laser source. An example of spectra that is obtained in this manner is shown in Figure 3. We see in this figure the signal in the vicinity of the R(3) absorption line. One will note from this spectrum that there is a photoacoustic signal produced by continuum absorption at the frequencies adjacent to the R(3) absorption line. This, unfortunately, will produce an additional photoacoustic signal when we attempt to detect the presence of the stimulated Raman effect when the down-pumping photon is added. It is known that there is a continuum signal underlying the Schumann-Runge band known as the Hertzberg Continuum [5]. We have found, however, that considerable additional continuum is generated due to the O_3 Hartley band. Ozone is produced from the dissociation of oxygen following the absorption of the 200 nm photon

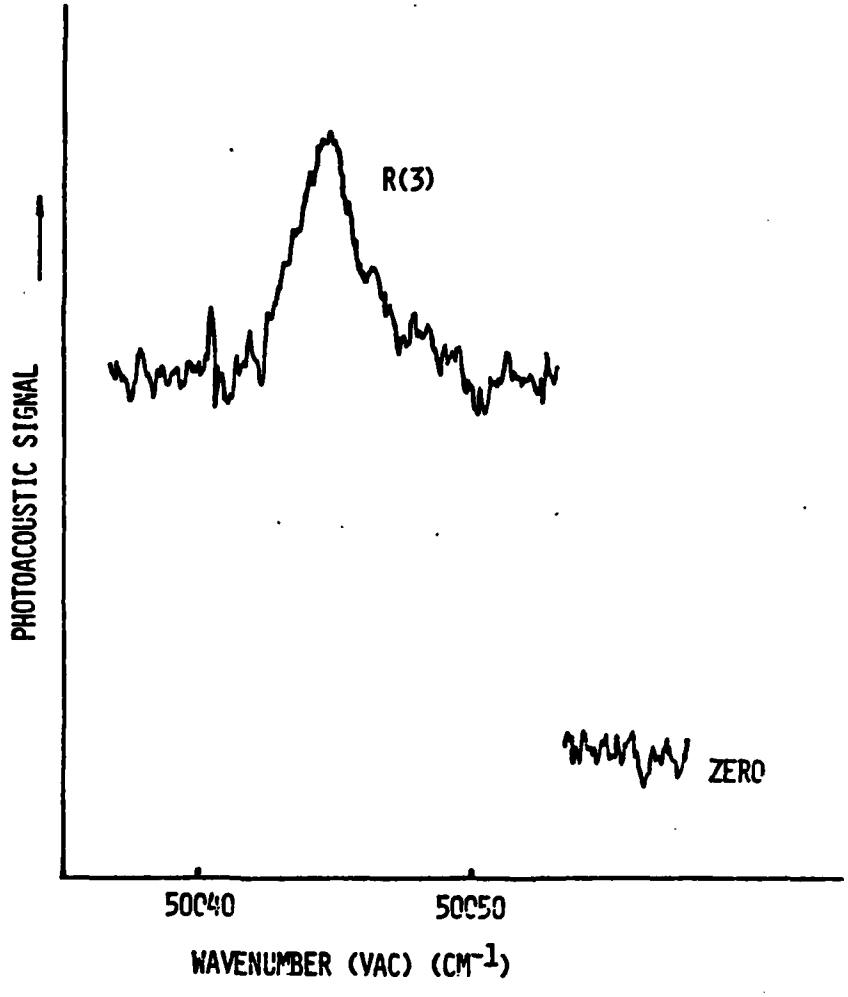


Figure 3. A photoacoustic spectrum of the 1-0 R(3) transition in the Schumann-Runge band of oxygen showing an additional continuum signal due to the Hartley band of O_3.

when the laser is tuned to the R(3) transition. This was proven by obtaining the spectrum of the gas mixture which was irradiated for some time with 200 nm radiation and the results of this are shown in Figure 4. Here we see the spectrum of the gas mixture in our photoacoustic cell at five different wavelengths superimposed on the known Hartley band spectrum [6]. It was found that this signal could be substantially reduced by utilizing a flowing cell to sweep out the ozone which is produced by each laser pulse. The predissociation of O_2 Schumann-Runge transition has been well characterized in the literature [7]. The lifetime effect of the predissociation leads to a broadening of the linewidths of the transitions as seen in Figure 5. We note here that this effect is minimized at the 1-0 transition region in which we are working.

The degree to which the predissociation of oxygen into ozone interferes with our ability to excite selected levels is unknown. In order to determine this we decided to first perform some overtone Raman and fluorescence measurements in an ordinary flowing Raman cell. In this manner we would minimize the generation of ozone and directly observe our ability to populate various levels of spontaneous processes. In the Raman apparatus which was described in the experimental section, we introduced the 200 nm radiation and analyzed the scattered light with a spectrograph. This light was detected with a EMI 6256 photomultiplier tube mounted at the output of the Spex monochromator. We utilized a Molectron boxcar signal averager synchronized with a Molectron YAG laser, plotted the amplitude of the output versus the wavelength with the laser fixed on the R(3) absorption line. A typical spectrum is shown in Figure 5. As can be seen in the figure, when the laser was tuned on resonance, scattered light was obtained from transitions to high-lying states of the ground electronic manifold. This indicates that a

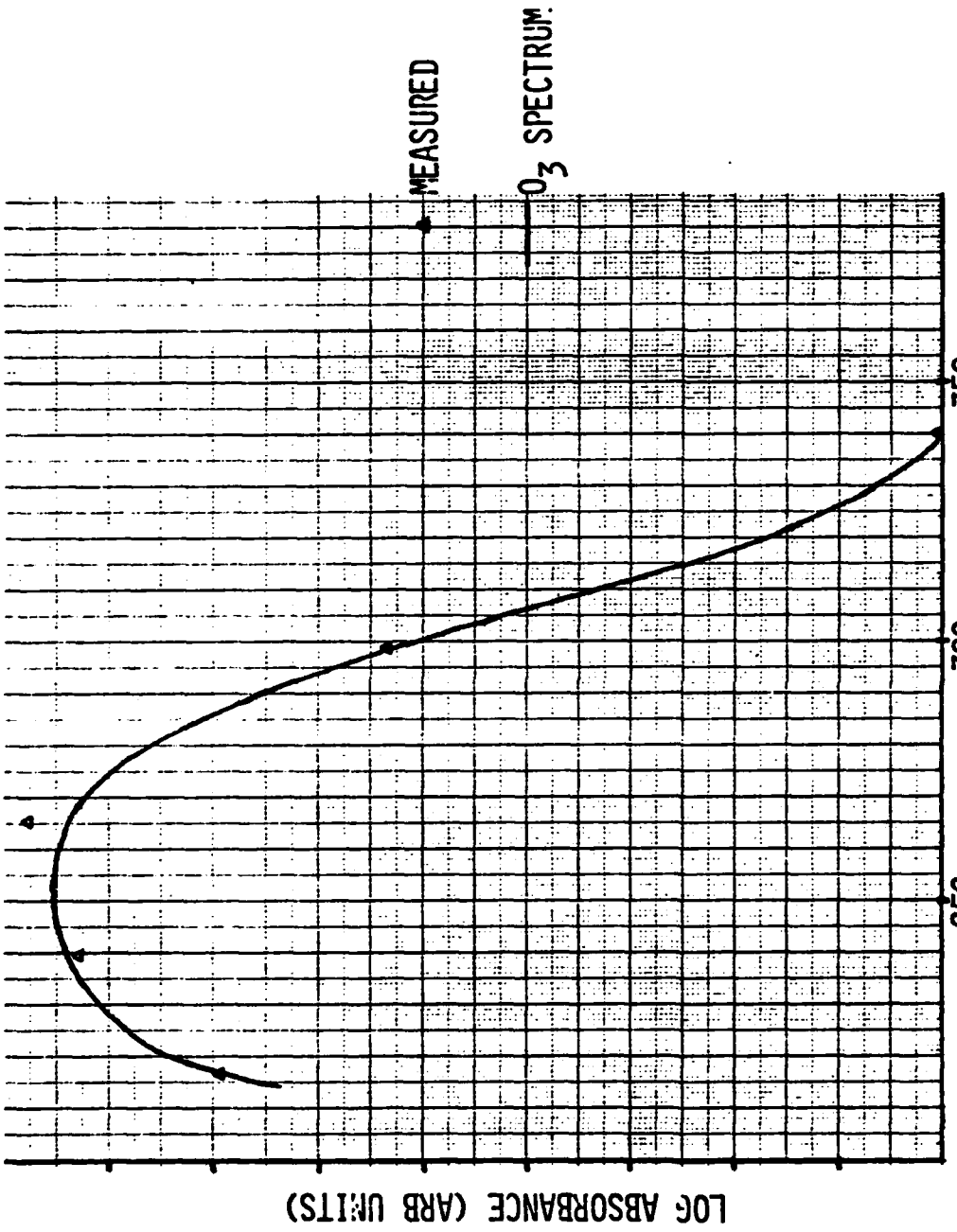
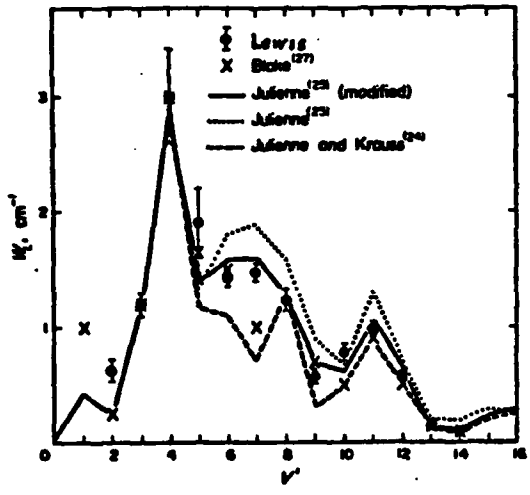


Figure 4. Absorption spectrum of the O_3 Hartley band compared with the measured absorbance of the material created in the O_2 photoacoustic cell.



$B^3\Sigma_u^-$ PREDISSOCIATION LINEWIDTHS W_L (CM^{-1}, FWHM)
(JQSRT 22, 213 (1979))

Figure 5. Predissociation linewidths in the O_2 Schumann-Runge band as a function of vibrational level of the upper state. The width of the line is proportional to the predissociation rate into oxygen atoms.

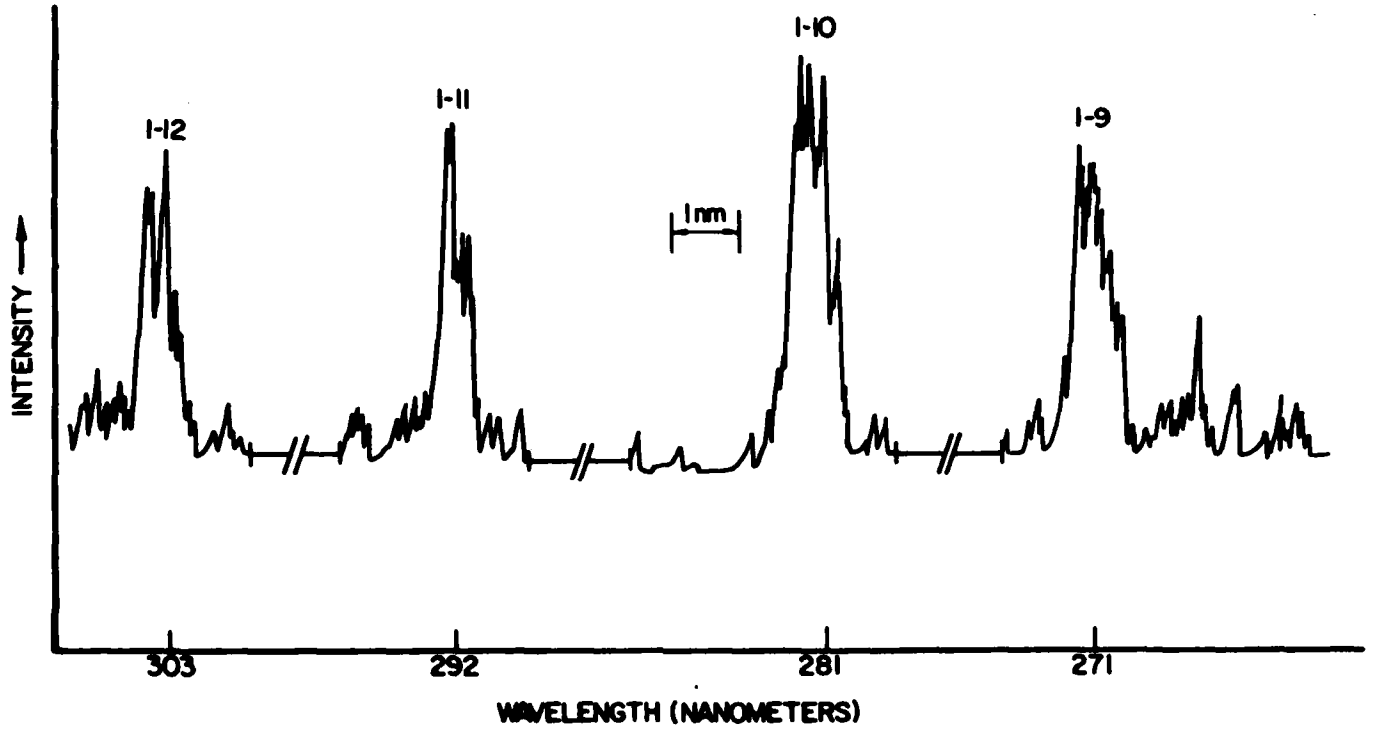


Figure 6. Intensity of fluorescence versus wavelength for O_2 pumped on the R(3) vibronic line in the 1-0 Schumann-Runge band.

significant number of oxygen molecules do not undergo predissociation but rather remain intact and return to excited states as we had hoped.

We are continuing to investigate the relative effect of the predissociation. This will be done by tuning the exciting laser off resonance and observing changes in the strength of the overtone transitions as compared to the predissociation rate. Since the photoacoustic signal is largely due to predissociation, by simultaneously passing the laser through a photoacoustic cell we are able to monitor the predissociation rate. We are also interested in the spectral character of the signal as the excitation laser is tuned of line center. One normally expects the signal to break into contributions from fluorescence and Raman processes. With predissociation leading to a strong quenching of the fluorescence the relative contributions of these two processes remains to be determined.

In summary, then, over the past two years we have designed a tunable ultraviolet laser system and coupled it with both Raman and photoacoustic diagnostics. These have been used to observe spontaneous overtone transitions to the oxygen ground electronic state due to resonant excitation. We have also constructed a tunable dye laser system capable of stimulating one of these transitions in order to selectively excite a particular state in the ground electronic manifold. The strong photoacoustic signal arising from the predissociation of the oxygen prohibits us from determining whether we are in fact significantly populating the state of interest. We are currently undertaking a series of spectral measurements to determine the relative strengths of predissociation, spontaneous fluorescence, and resonant Raman.

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5. GRADUATE STUDENTS AND POSTDOCTORAL PERSONNEL ASSOCIATED WITH THIS CONTRACT

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